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DEVELOPMENT OF LOW COST CONTACTS TO SILICON SOLAR CELLS

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By

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JPL CONTRACT NO. 955244

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ABSTRACT

This report states the results of the second phase of the program of developing low cost contacts to silicon solar cells using copper. Phase I yielded the development of a plated Pd-Cr-Cu contact system. This process produced cells with shunting problems when they were heated to 400°C for 5 minutes. Phase II was to find means of stopping the later identified copper diffusion which caused the shunting. A contact heat treatment study has been conducted with Pd-Ag, Cu-Ag, Pd-Cu, Cu-Cr and Cu-Ni-Cu. This study has shown nickel to be an effective diffusion barrier to copper.

To decrease the cost of the contact system it has been thought that nickel should replace the chromium in the old process. This is the route the last part of the program will take.

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INTRODUCTION*

The contract involves evaluation of the technical feasibility and effective cost of a copper plating system for the manufacture of solar cells for high volume production of low cost solar array (LSA) modules. The LSA goal is to provide low cost silicon solar cells formed into operational arrays. At present, the cost breakdown shows that about 1/3 of the array cost is in materials (silicon and metals), slightly more than 1/3 for processing into cells, and the remainder for array formation. Much of the LSA effort (Tasks 1, 2) is aimed at reduced silicon cost; other effort in Task 4 is aimed at process cost reduction and at automated processing. Other efforts are directed towards cell interconnection and encapsulation. Already the projected silicon costs show promise of reaching the near-term LSA goals, although as the minimum array efficiency goals are increased, more attention is being paid to the adequacy of lower cost silicon for use in high efficiency arrays. In most cases, it appears that the silicon cost goals may be achieved. Also many of the individual cell process steps appear to be capable of cost reduction to fit the goals.

The major process costs are those involved with the metallization required to contact and interconnect the cells. The costs of metals is rising, and with present understanding it appears that at least 1.6×10^{-4} cm³ of good conductivity metal will be needed for each cm² of cell area; this is an irreducible cost factor. It is, however, important to provide

*For convenience, repeated from First Quarterly Report.

this minimum amount of metal with as little waste (or even reclaimable) metal as possible. It is for this reason that careful analysis is proceeding on vacuum evaporation systems (where over 90% waste metal is used in depositing fine metal pattern), or of silk screened systems, where equivalent excesses are involved, although with greater ease of re-use.

Of all present methods, plating is most attractive in reduced metal usage; with resist patterns applied to the cell surface to leave the required areas available for metallization, it is possible by plating to deposit metal only where required. Thus metal usage can be kept to a minimum, and in addition the fact that a high vacuum is not required makes plated contacts most promising for reduced costs.

There are other aspects of contacts which must be considered. To date, most of the field failures have been attributed to the cell contacts, either because of reduced cell efficiency following thermal cycling, or after corrosion caused by exposure to the atmosphere. The latter problem can be reduced by improved encapsulation methods.

For metals such as copper there are additional concerns regarding possible cell degradation should the copper migrate into the cell. The degradation could be from reduced diffusion length (reduced I_{sc}) or possible shunt mechanisms, decreasing both CFF and V_{oc} .

With the above background, it is clear why plated systems merit study in the present program, and also why the required precautionary and proving-out tests have been included.

PAST WORK (PHASE I)*

During Phase I of the contract (15 October 1979 to 31 May 1979) a plated contact sequence was developed which used copper as the main conductor. The sequence first used an immersion palladium bath[§] which deposited ~50Å of palladium. Next an electroless chromium bath deposited ~2000Å of chromium on the palladium sensitized areas of the cells. Last an electroless copper bath deposited ~500Å of copper on the chromium and was followed by an electrolytic copper step to deposit 3-4 microns of copper. Cells with good I-V curves as well as good contact adherence were made (see Figure 1). All cells made used a phosphorus diffused 7-14 ohm-cm p-type (100) oriented silicon with an aluminum alloyed BSF. The first cells were 2x2 cm in area but later the process was scaled up to 2½" cells. These first cells had their contact patterns defined by photoresist techniques which were shown to be expensive for our process goals (1). Forty (40) 2½" diameter cells of this final process were delivered to JPL at the end of the first phase of the contract. Typical solar cell efficiencies of this group of cells are shown in Table 1 and Figure 2.

At the end of Phase I it was also shown that heat treatments of this contact system (~400°C - 5 minutes) would cause severe shunting problems possibly due to copper diffusion into the cells (1). This problem is the major reason for barrier studies in Phase II of the contract, to try and find means of stopping the copper diffusion.

*For convenience, repeated from Second Quarterly Report.

§See Appendices for full procedures for the processes.

FIGURE 1

Plated Palladium-Chromium-Copper

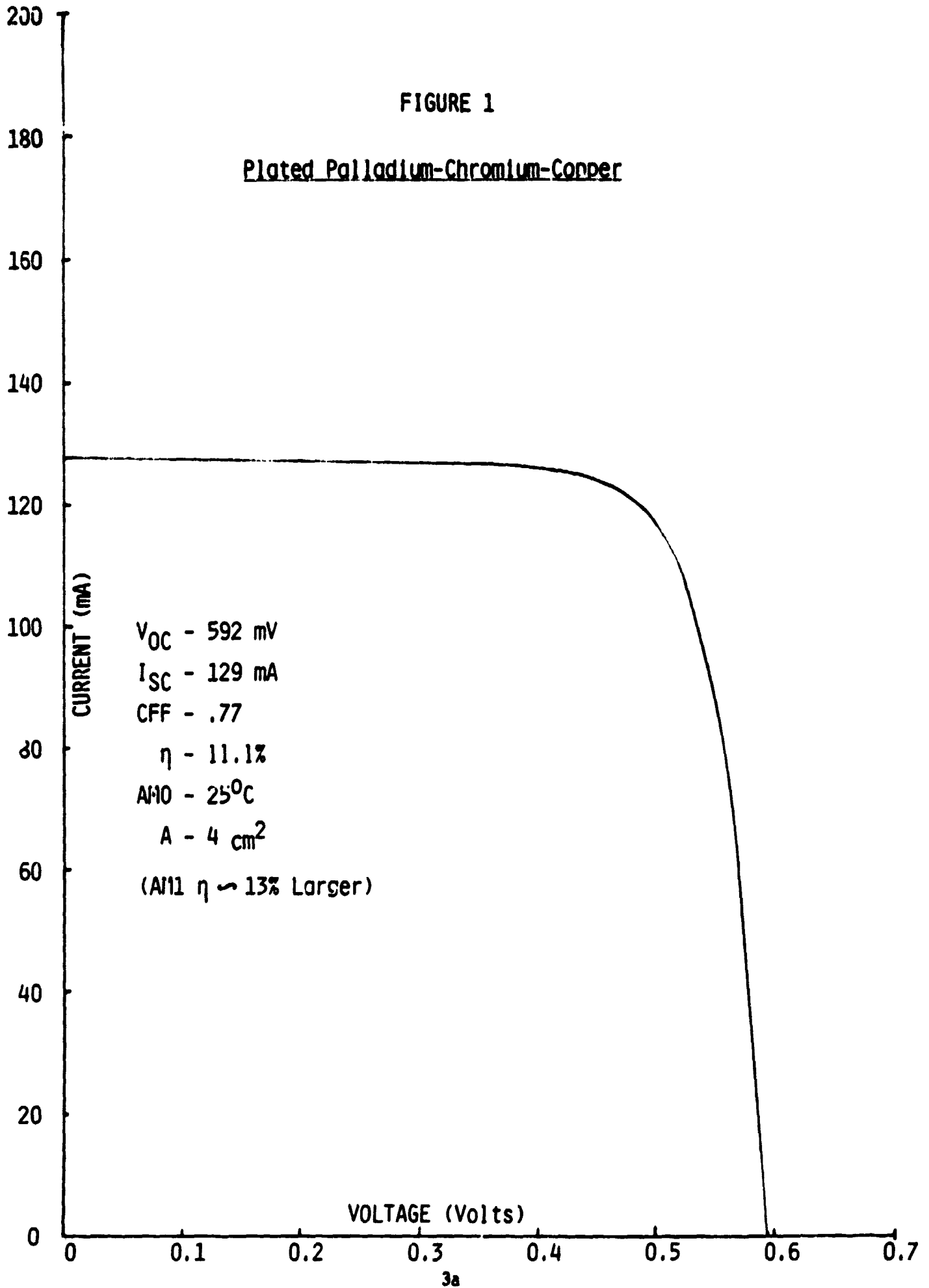


TABLE 1

CELL DESCRIPTION:

TEST CONDITION:

TEMPERATURE:

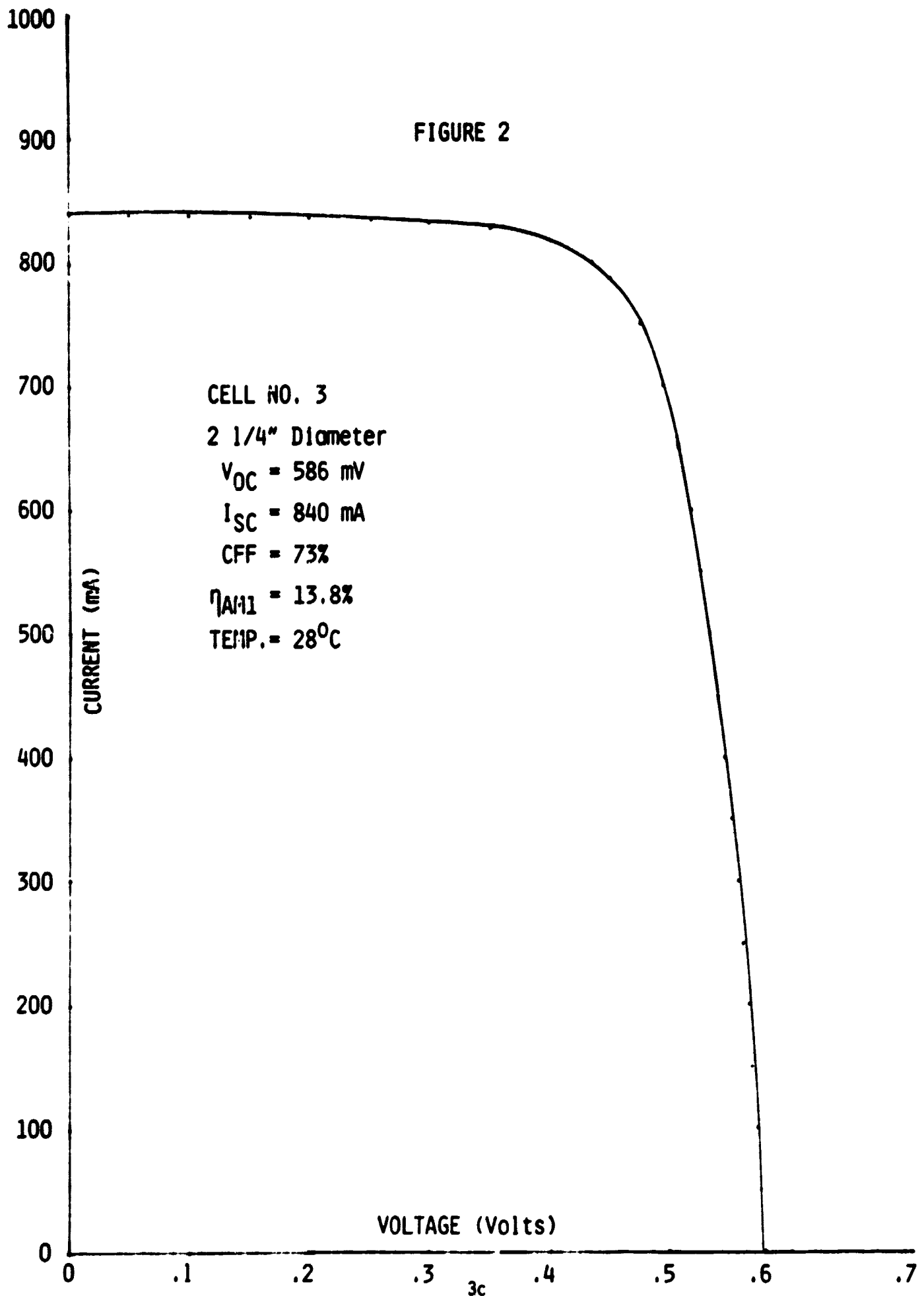
DATE: 15 May 79

NO.	V _{OC}	I _{SC}	I _{SCB}	I _{SCR}	I _{Max}	V _{Max}	P _{Max}	CFF	n	AREA
	mV	mA	mA	mA	mA	mV	mW	%	%	cm²
1	586	840	---	---	750	470	352.5	72	13.7	25.7
2	585	850	---	---	755	470	354.9	71	13.8	25.7
3	579	840	---	---	755	470	354.9	73	13.8	25.7
4	454	817	---	---	550	260	143	39	5.6	25.7
5	586	868	---	---	760	460	349.6	69	13.6	25.7

Cells had only approximately 30% current increase due to the CVD SiO₂ (only a plating mask). These are five cells taken in random from the forty (40) cells delivered to JPL.

[illegible]

FIGURE 2



PRESENT WORK (PHASE II)

Paper Study

A literature search was conducted to locate papers dealing with copper diffusion and/or interactions with different metallic barriers. A summary of the data is given in Figure 3. Nickel was indicated as the best inexpensive platable barrier to copper diffusion. The next step was to test this conclusion experimentally.

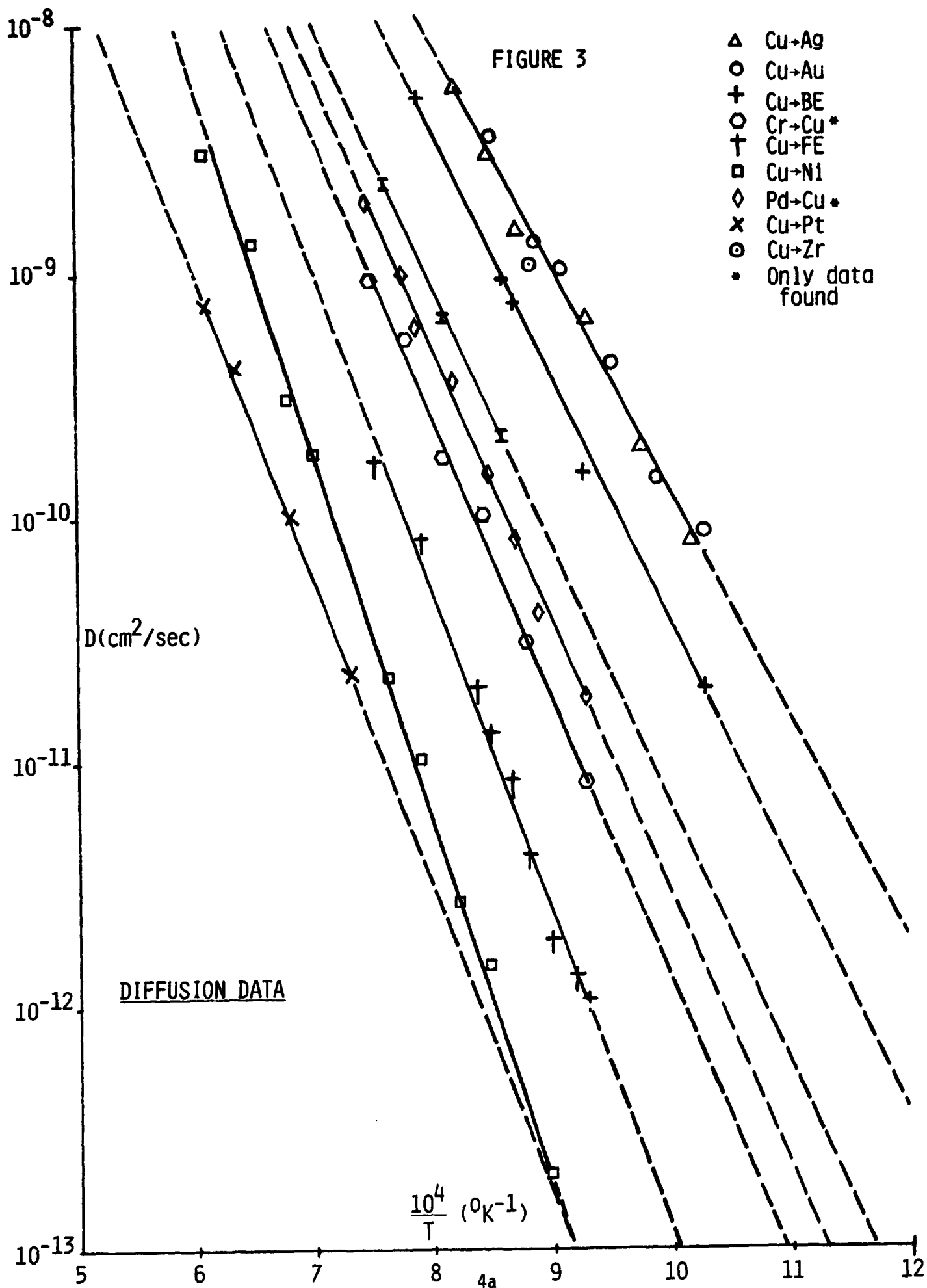
Heat Treatment Study

A heat treatment study using evaporated metals designed to test the results of the paper study was initiated and completed. The study monitored the V_{OC} , CFF and I_{SC} of active solar cells for degradation effects caused by the heating. Early experiments (1) had shown that when copper diffuses into an active solar cell, there is an immediate decrease in the cell V_{OC} without any change in the I_{SC} (with the expected decrease also of the curve fill factor). The purpose of this study was to check experimentally if nickel is a good barrier to copper. The test matrix details were as follows:

- (i) All heat treatments were done in nitrogen only.
- (ii) Properties of the solar cells were evaluated before and after the heat treatments.
- (iii) Heat treatment details:

Times (Minutes)	Temperatures (°C)				
5	400	450	500	550	600
15	400	450	500	550	600

- (iv) Cell tests included control cells using Ti-Pd-Ag contacts.



Results from several contact systems were previously reported (3). Figure 4* shows the change of the V_{oc} (of 2000Å - thick Ag contacts) with heating, as compared to the Ti-Pd-Ag control cells. This system appears stable to about 500°C. Figure 5 shows the change of V_{oc} for 2000Å Cr - thick silver contacts, as compared to the Ti-Pd-Ag control cells. This system appeared stable to about 550°C. Also a test was done using 1000Å Pd and 3 microns of copper (Figure 6). The cells were severely degraded even for the 400°C heat treatment. From the paper study the diffusion data predicted that at 560°C, a 1000Å Pd layer would only protect the silicon from the copper for 51 seconds using a single mode diffusion calculation. Thus these results seem reasonable. Further experiments were not completed for 2000 and 3000Å Pd layer tests due to the fast diffusion time of this contact system. On all tests the short circuit current was monitored and relatively no change was seen over the entire temperature range. This would indicate that if copper diffused into the silicon it did not cause any bulk lifetime reduction.

For the next set of tests, more data was added to better understand the changes the devices were exhibiting during the heat treatments. The tests were expanded to measure V_{oc} and I_{sc} , the curve fill factor (CFF), and the dark forward I-V characteristics before and after the heat treatments. First chromium copper contacts were studied using three different thicknesses of chromium, 1000Å, 2000Å, and 3000Å. Figure 7, 8, and 9 show

*Note: The points plotted on Figure 4 (and following Figure 5 through 18) represent the average measured for 5-cell groups.

the results of five minute heat treatments. The cells with 2000 or 3000A chromium appeared to be stable to temperatures as high as 550°C. Notice the change in CFF and in dark current at .3 volt data (Figures 8 and 9) data support the ΔV_{OC} data (Figure 7). Figures 10, 11 and 12 show the results of the 15 minute heating for the chromium-copper system. Again the 2000A and 3000A layers of chromium held up better than the 1000A chromium layer cells. Perhaps the 1000A layer cells had more pinholes or surface cracks. The 2000A and 3000A chromium layers cells performed well until ~500°C. At higher temperatures all three plots indicated severe degradation of the cells.

The next contact system that was studied was chromium-nickel-copper. The chromium was applied only in a 2000A layer whereas the nickel was used in 1000A and 2000A thicknesses. For the five minute heat treatments the contact system performed well to 550°C and only showed a small amount of degradation at 600°C. These results are shown in Figures 13, 14 and 15. Figures 16-18 show the graphical results of the 15 minute study. The cells performed well to 500°C; also cells that had a 2000A nickel layers performed better than the Ti-Pd-Ag controls at 600°C. It appears that even when the Cr-Ni-Cu cells start to degrade (~500°C) the degradation rate is slower than with the Cr-Cu cells. These results confirm that nickel is a good barrier to copper diffusion.

Experiments were also made to study the Pd-Ni-Cu system. This work would explicitly show the barrier qualities of nickel, since palladium is such a poor barrier. Palladium does not stick to the silicon surface very well and when the highly stressed nickel layer was deposited the contacts

FIGURE 4

2000Å Pd - Thick Ag

○: 5m Control
 ●: 15m Control
 +: 5m Pd-Ag
 □: 15m Pd-Ag

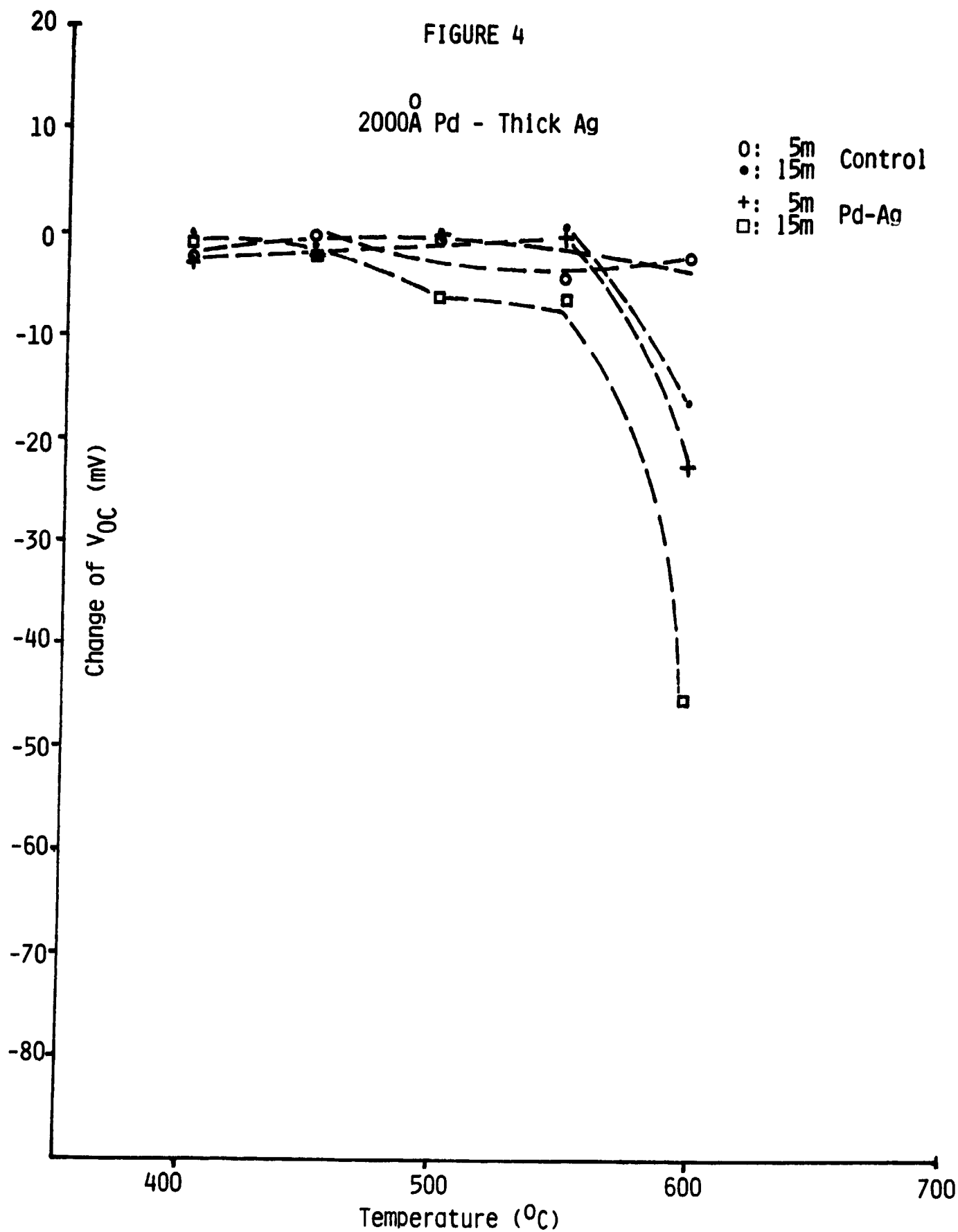


FIGURE 5

⁰
2000Å Cr - Thick Ag

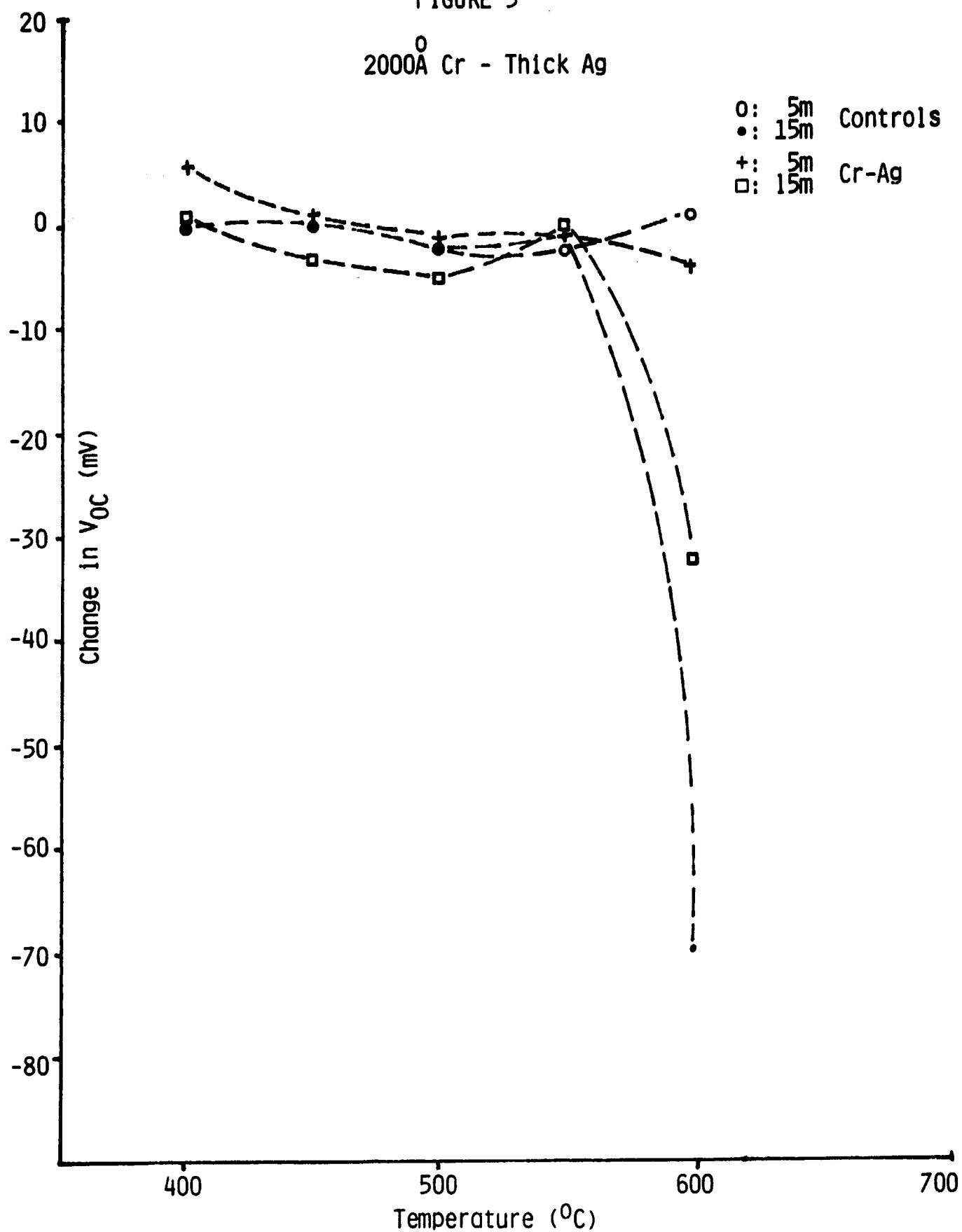
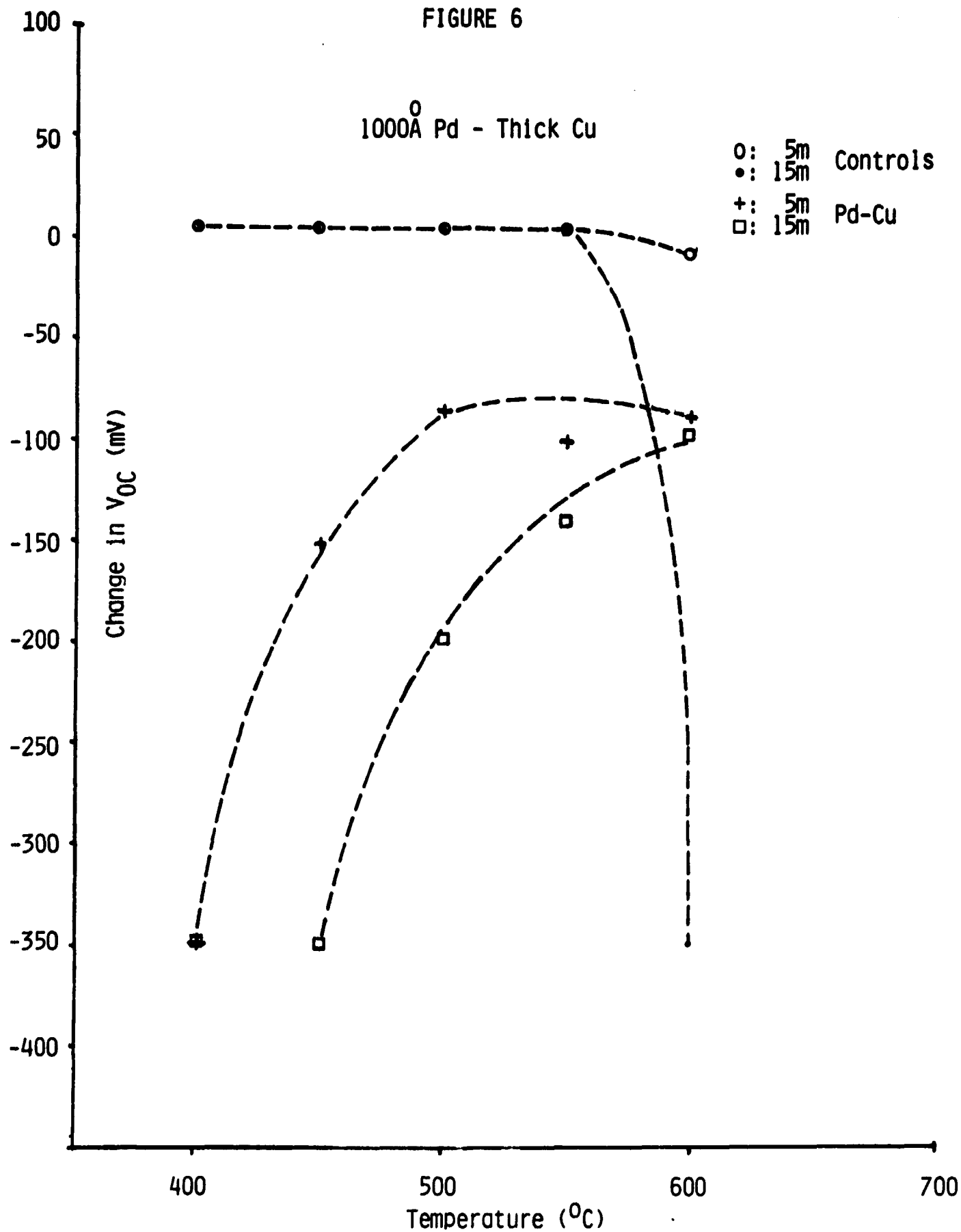


FIGURE 6

1000Å Pd - Thick Cu

○: 5m Controls
 ●: 15m Controls
 +: 5m Pd-Cu
 □: 15m Pd-Cu



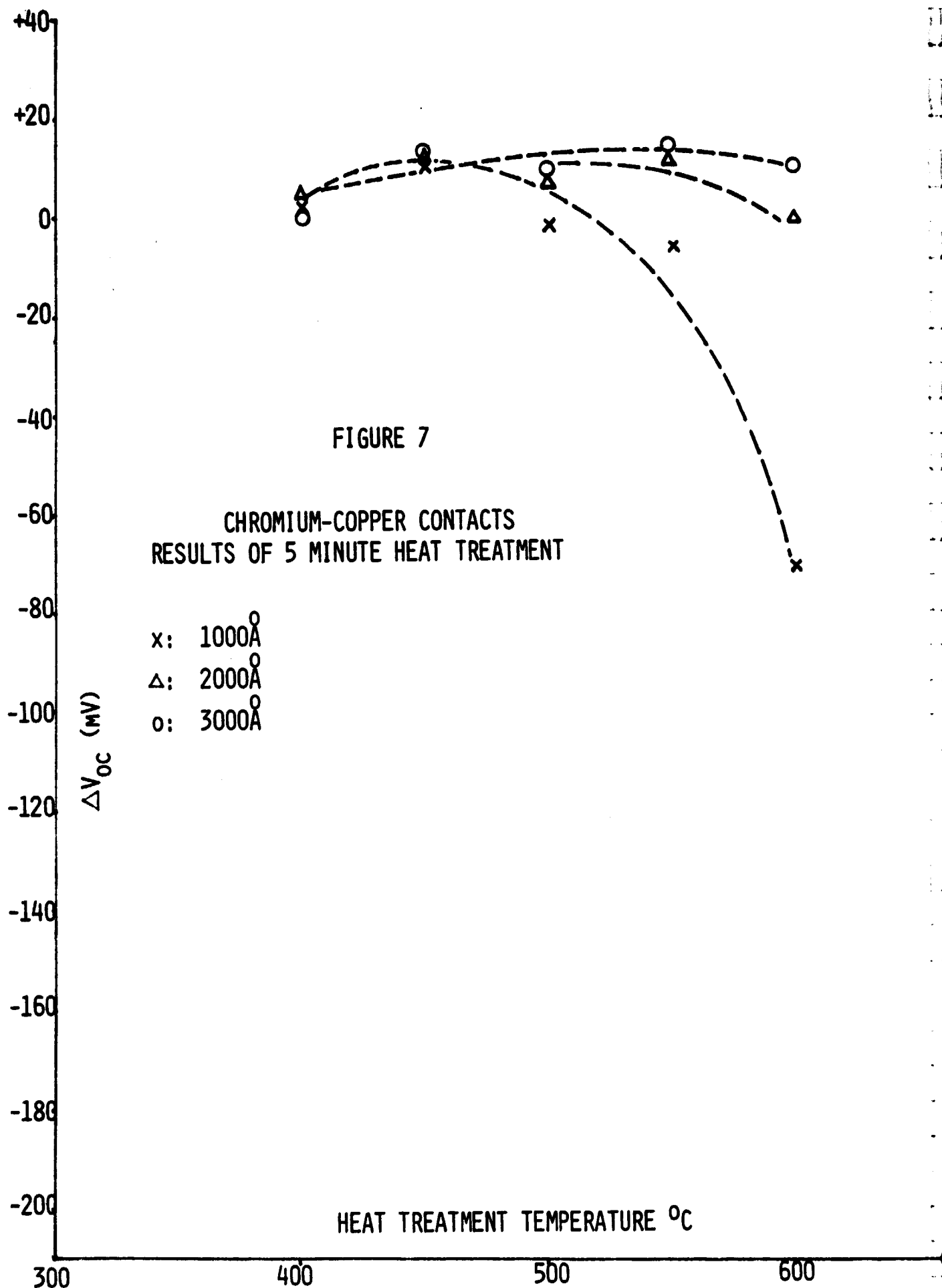


FIGURE 8

CHROMIUM-COPPER CONTACTS
RESULTS OF 5 MINUTES HEAT TREATMENTS

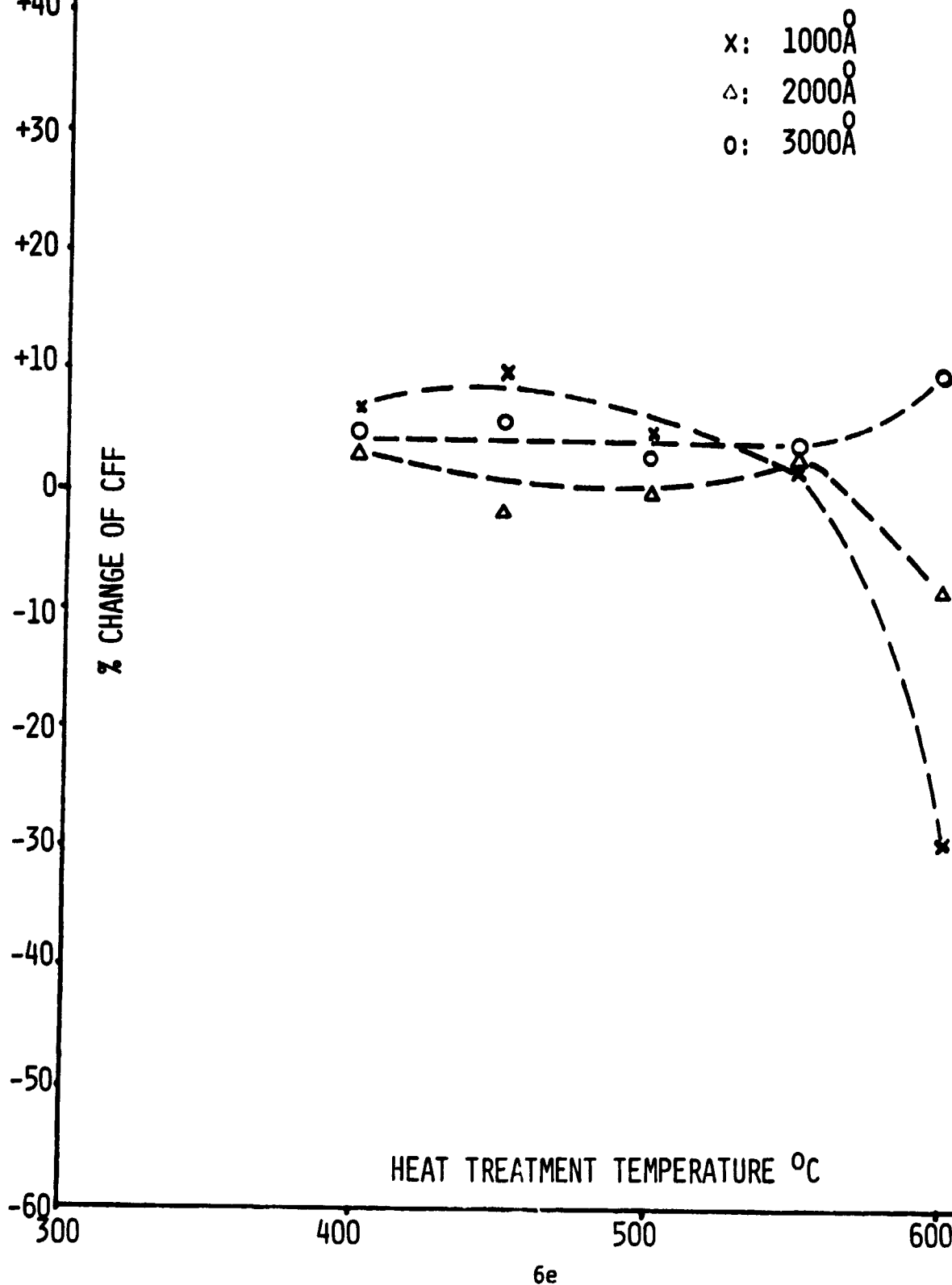


FIGURE 9

CHROMIUM-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT

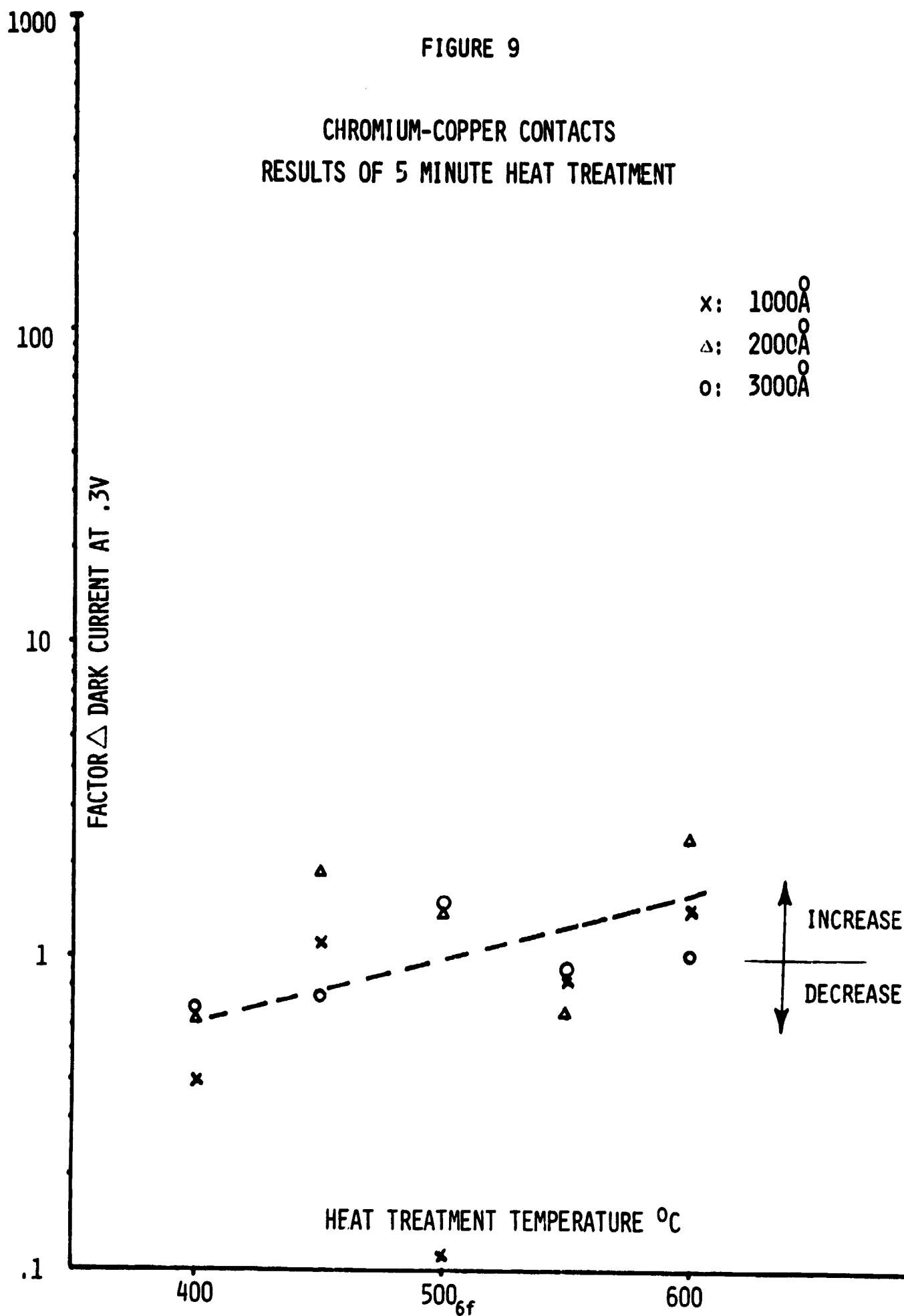


FIGURE 10
CHROMIUM-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

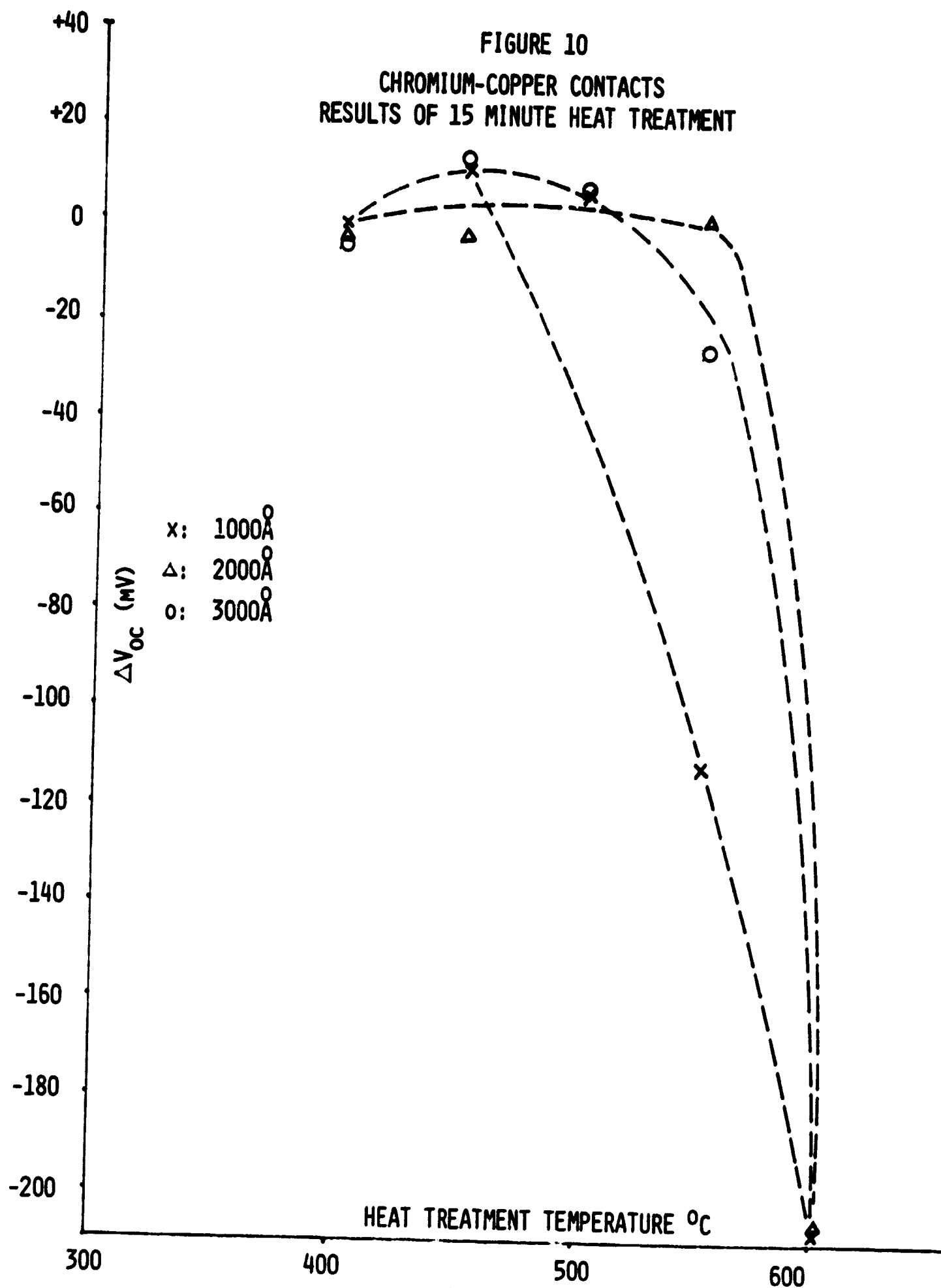


FIGURE 11

CHROMIUM-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

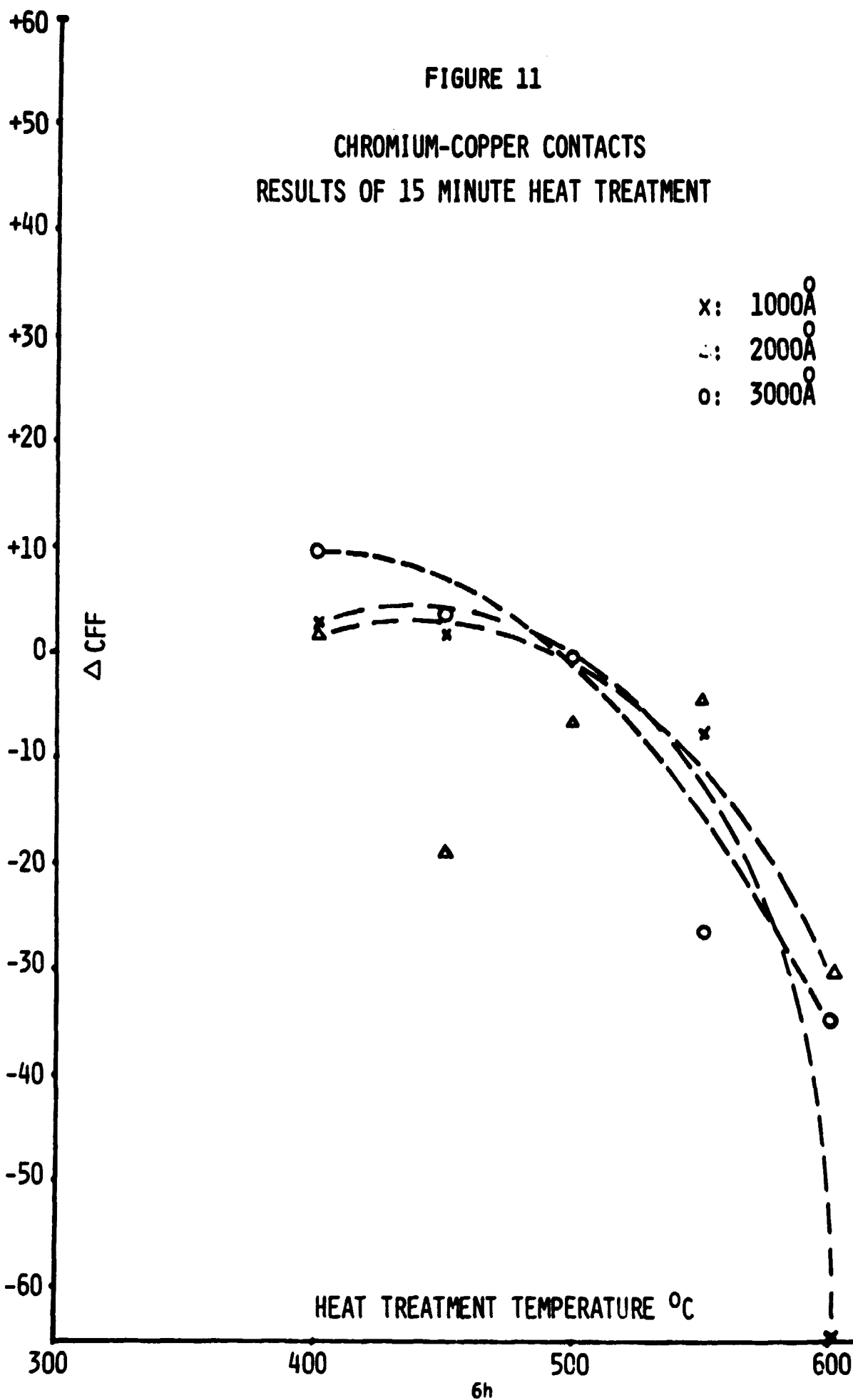


FIGURE 12
CHROMIUM-COPPER CONTACT
RESULTS OF 15 MINUTE HEAT TREATMENT

FACTOR Δ DARK CURRENT AT .3V

x: 1000Å
Δ: 2000Å
o: 3000Å

INCREASE
DECREASE

HEAT TREATMENT TEMPERATURE °C

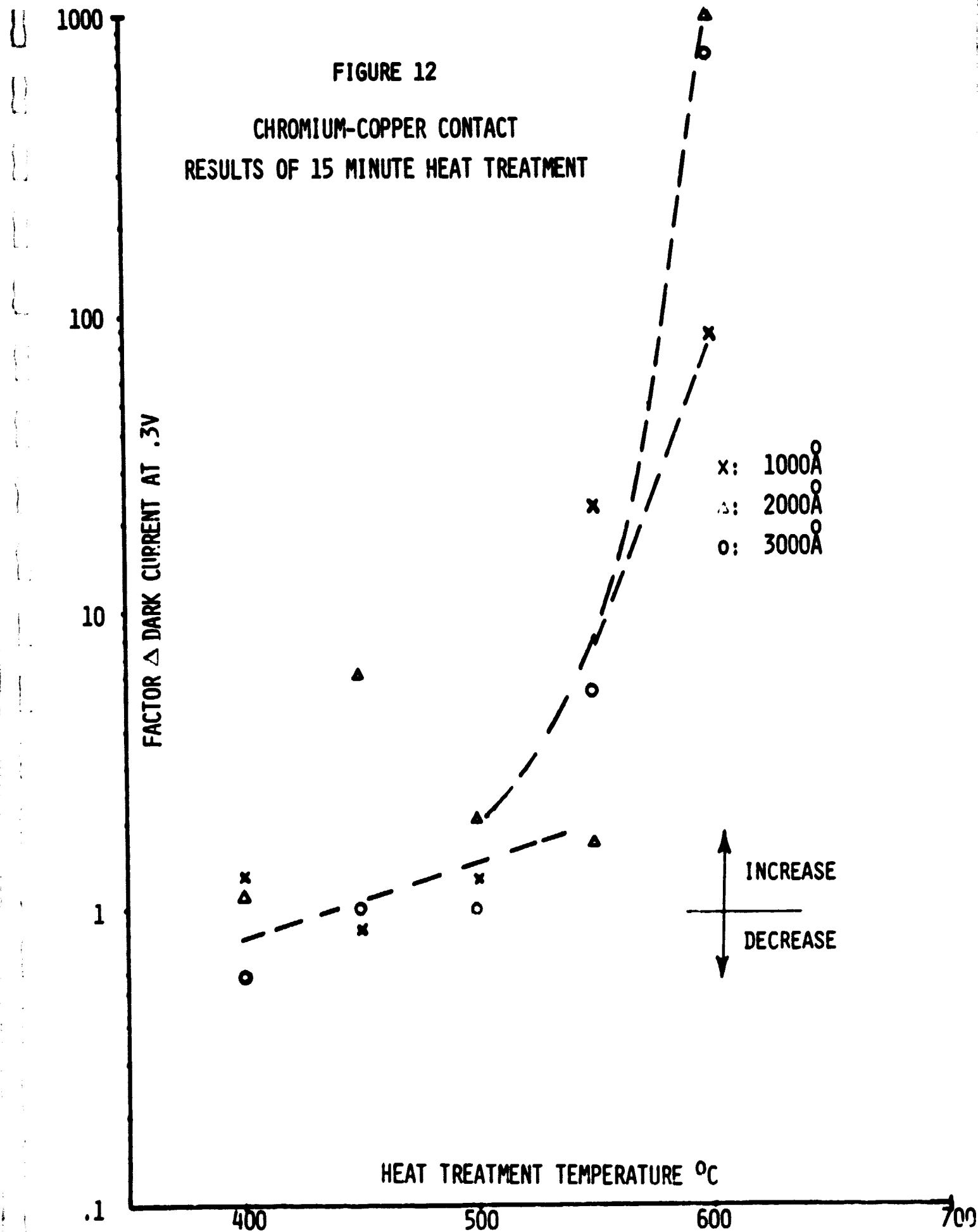
.1

400

500

600

700



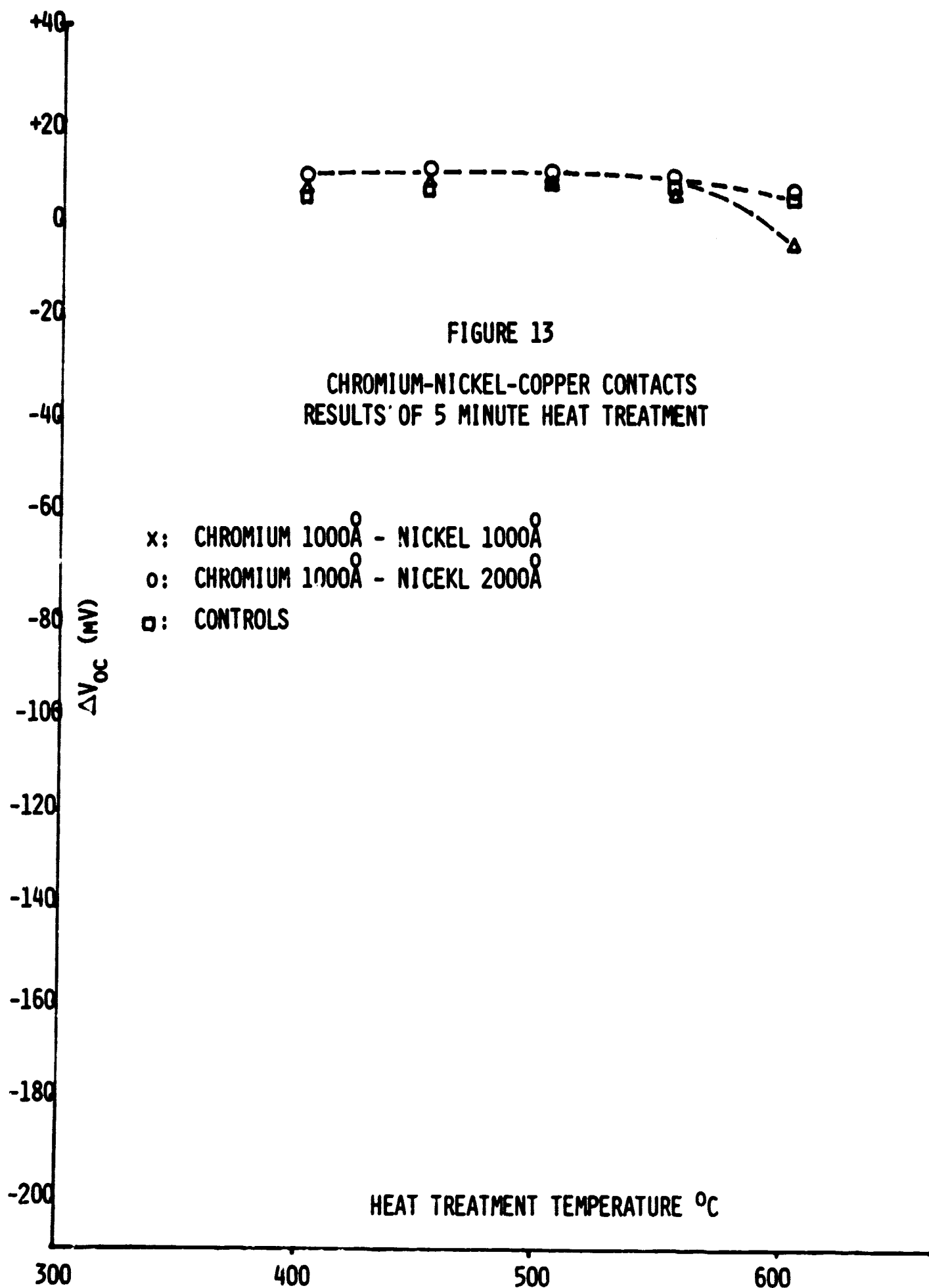


FIGURE 14

CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT

△: CHROMIUM 1000Å - NICKEL 1000Å
○: CHROMIUM 1000Å - NICKEL 2000Å
□: CONTROLS

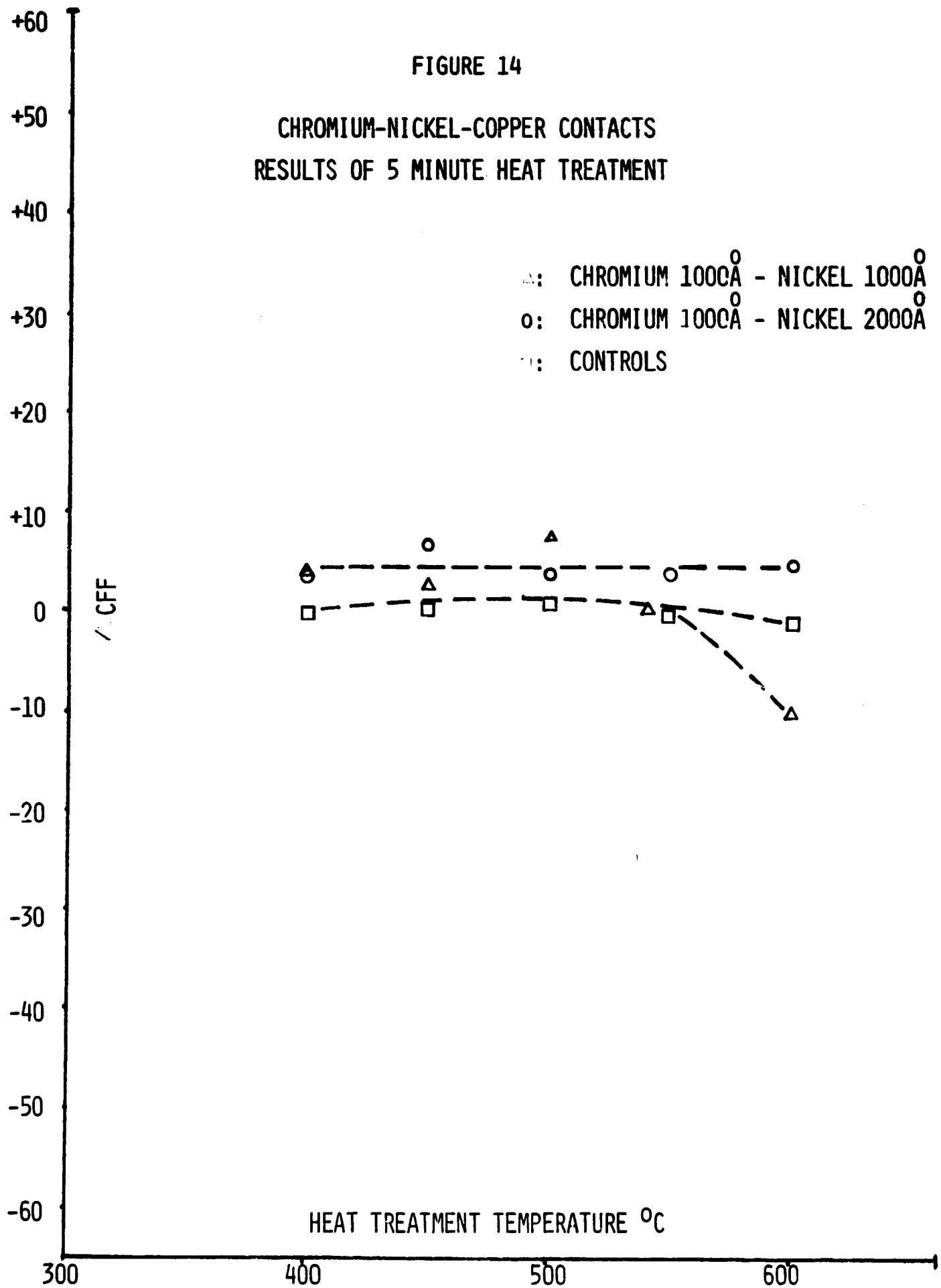
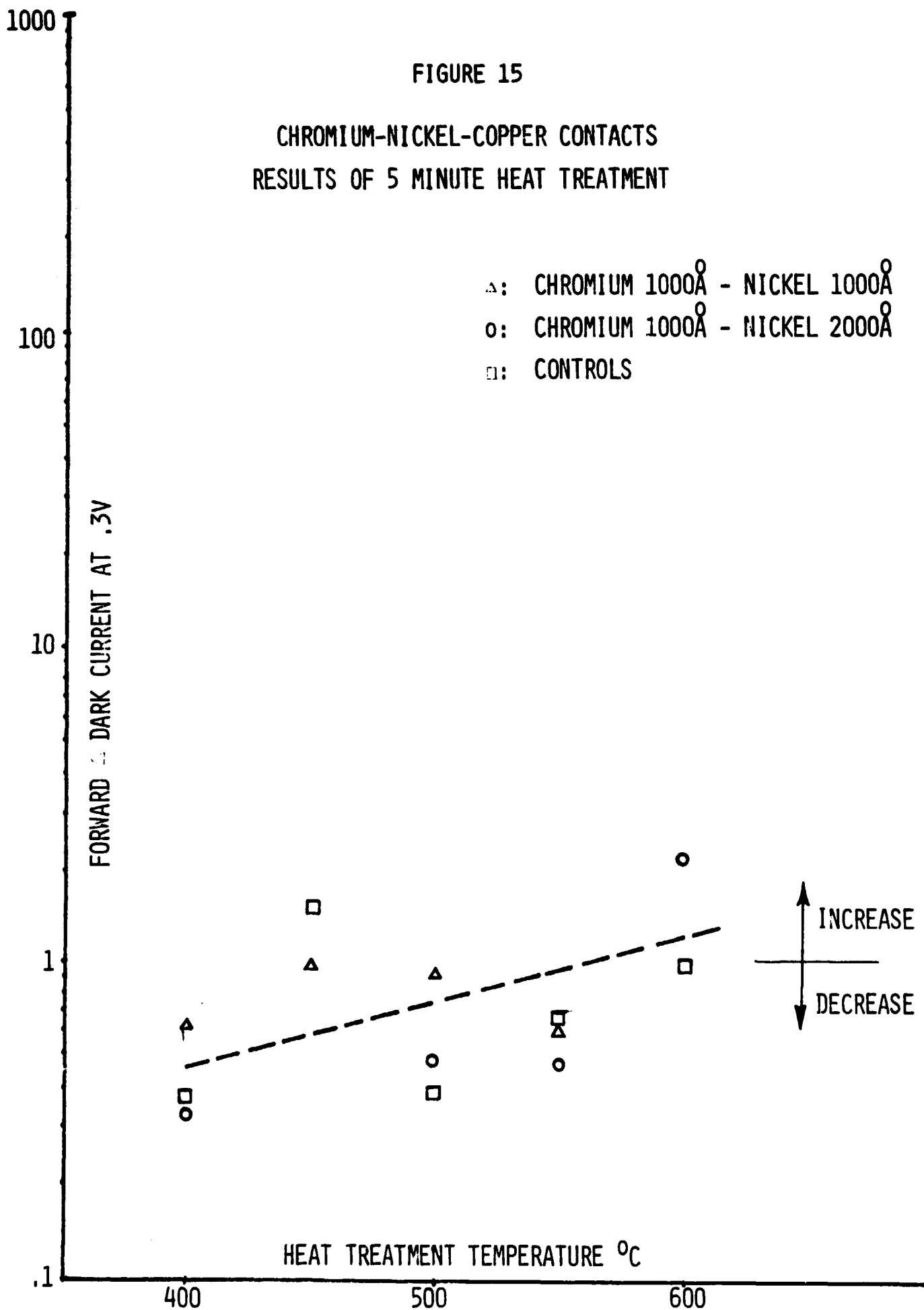


FIGURE 15

CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT

- Δ: CHROMIUM 1000Å - NICKEL 1000Å
○: CHROMIUM 1000Å - NICKEL 2000Å
□: CONTROLS



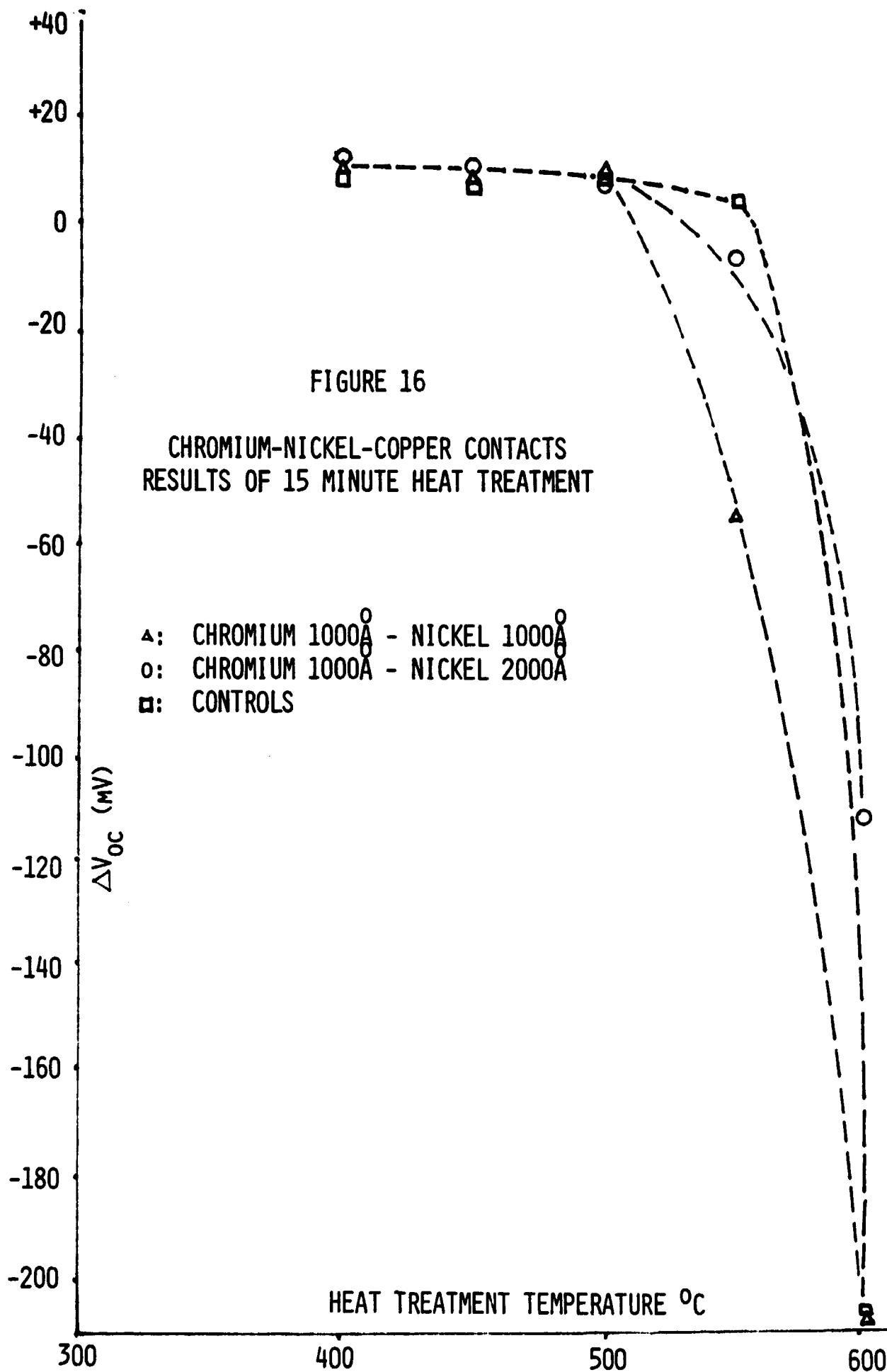


FIGURE 17
CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

△: CHROMIUM 1000Å - NICKEL 1000Å
○: CHROMIUM 1000Å - NICKEL 2000Å
□: CONTROLS

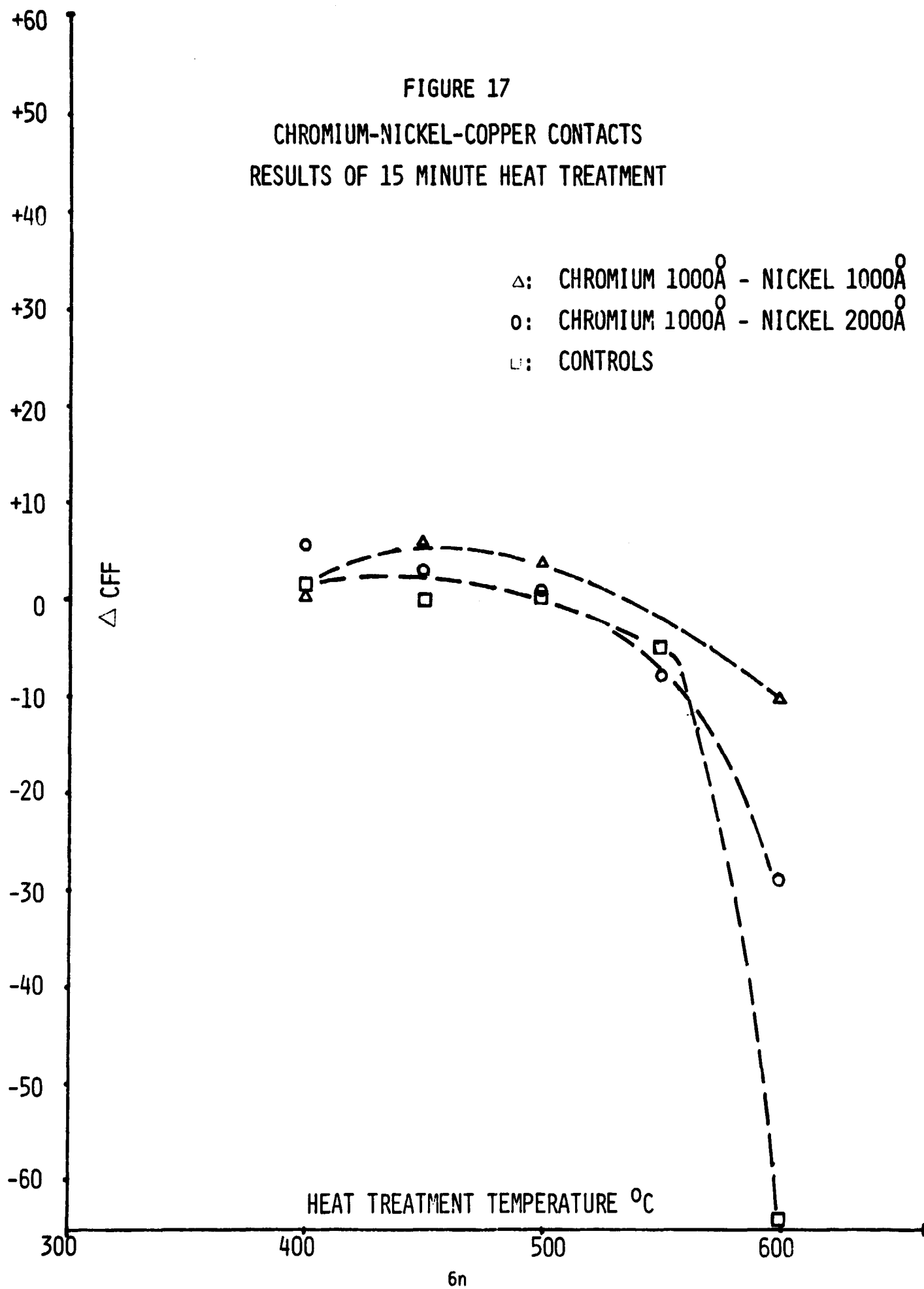


FIGURE 18

CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

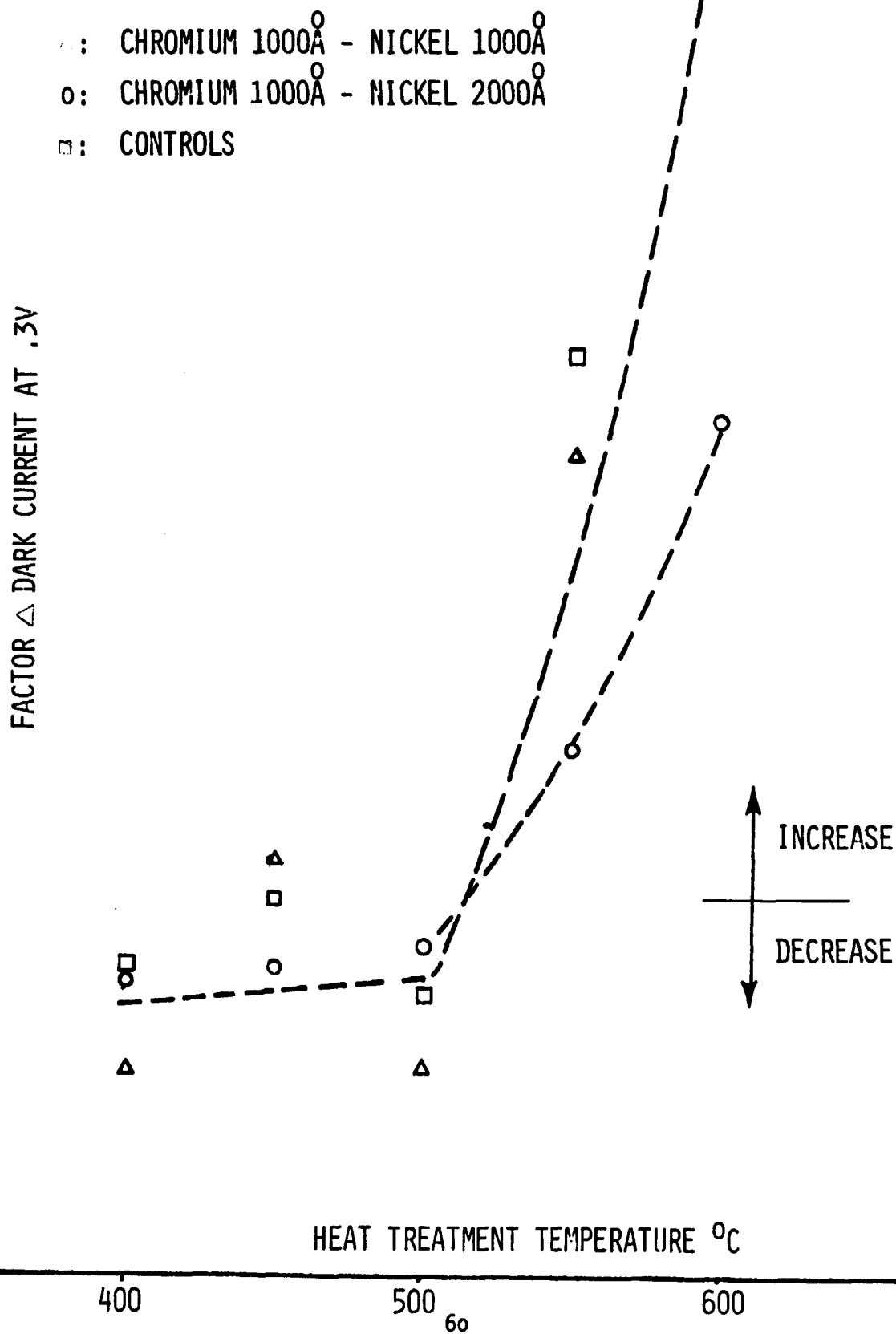
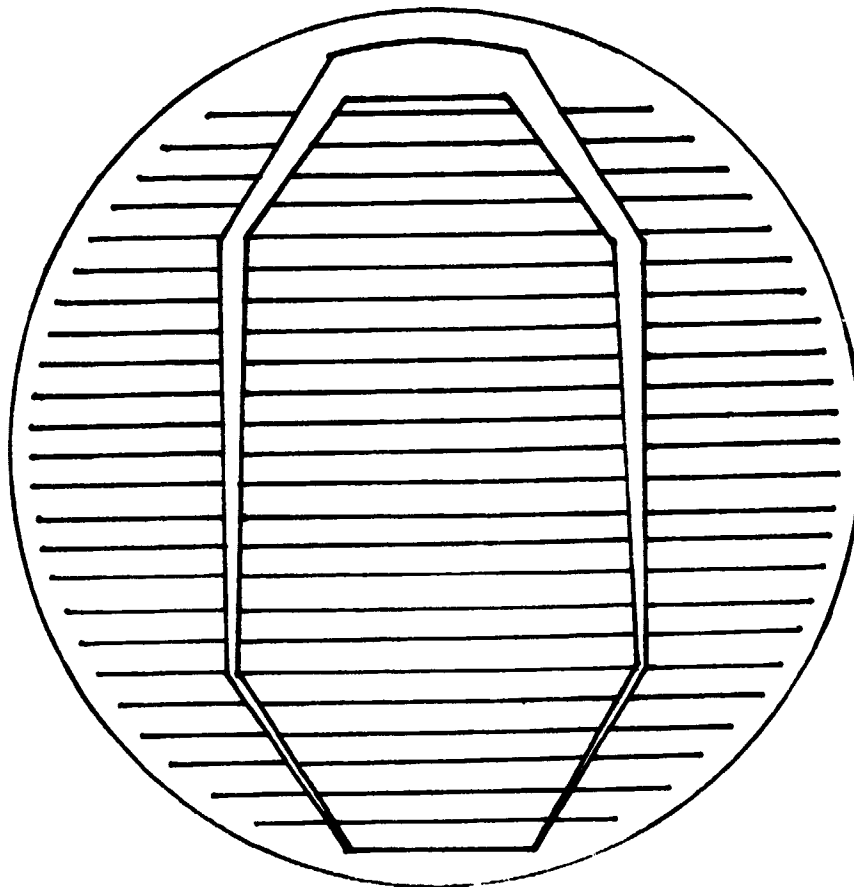


FIGURE 19

2 1/4" Diameter Contact Pattern

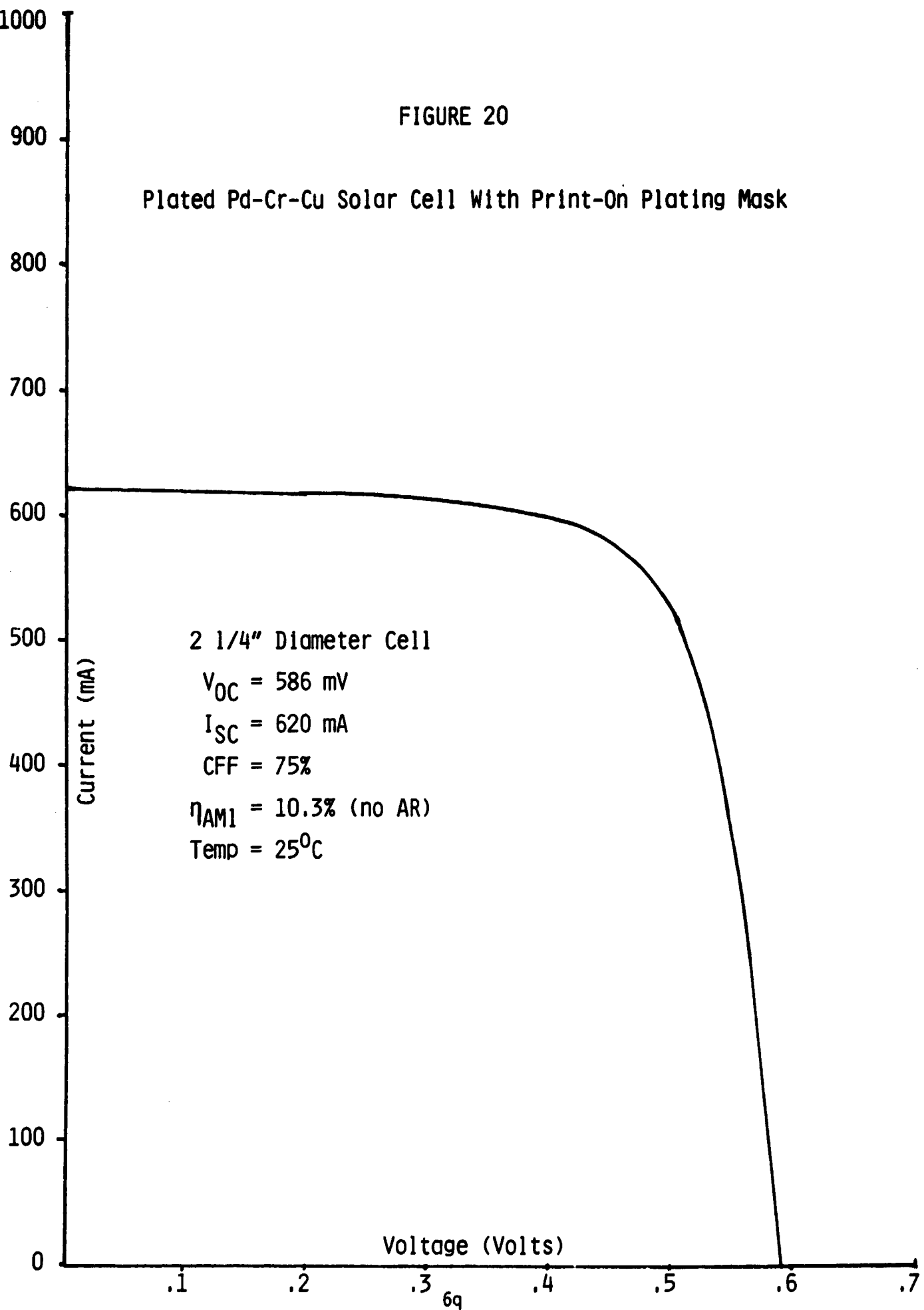


Contact Coverage: 12%

Grid Line Thickness: <5 mil

FIGURE 20

Plated Pd-Cr-Cu Solar Cell With Print-On Plating Mask



lifted off. Therefore no reasonable results were obtained for Pd-Ni-Cu contacts.

Print-On Plating Mask

An important aspect of any plating work is how the metal is patterned on the cell. Earlier in the program photoresist techniques were used to define the cell contact patterns. This method was found to be too expensive. As an alternative approach a screen printable mask was found which performed well in the plating baths. As with most low cost approaches some resolution of the grid lines is lost; even so, grid lines of less than 5 mils have been made with this resist. Figure 19 shows a contact pattern developed for 2½" diameter cells. This pattern gave a measured contact coverage of 12% using 5 mil grid lines. Figure 20 shows a typical I-V plot of a cell using this pattern mask and plated Pd-Cr-Cu contacts. See Appendix F for screening procedures.

FUTURE WORK (PHASE III)

In the Phase II program it was thought that a copper barrier would be found and could be incorporated in the old plating sequence Pd-Cr-Cu. Since nickel was found the new sequence would be Pd-Cr-Ni-Cu. But it was clear that this is not the most cost effective route. Palladium-nickel-copper contacts have been tried and showed reasonable promise. Presently a commercially available nickel solution is being used. To further simplify the process, new nickel baths will be tried in our effort to eliminate the Pd bath.

Also the process will be scaled up to accommodate 3" diameter cells. At the end of the contract 150 cells of mostly 3" size will be delivered to JPL. A new silk screen has been received for the 3" diameter cells and no problems have been found in the scaling up process.

CONCLUSIONS

Nickel has been experimentally proven to be a good barrier to copper diffusion. Coupled with the new print-on mask, cells have been made that show reasonable characteristics, and promise of stability under long-term use (judged by results of accelerated heating tests).

WORK PLANNED

A number of nickel plating baths will be studied to find a bath that yields a nickel layer with better adhesion than the bath presently used. When the final process sequence is found a larger number of cells will be made. From these cells a heat treatment study will be conducted to assess the reliability of these cells.

NEW TECHNOLOGY

New processes have not been sufficiently developed to be reported as new technology. Any new developments will be described at completion of the contract.

REFERENCES

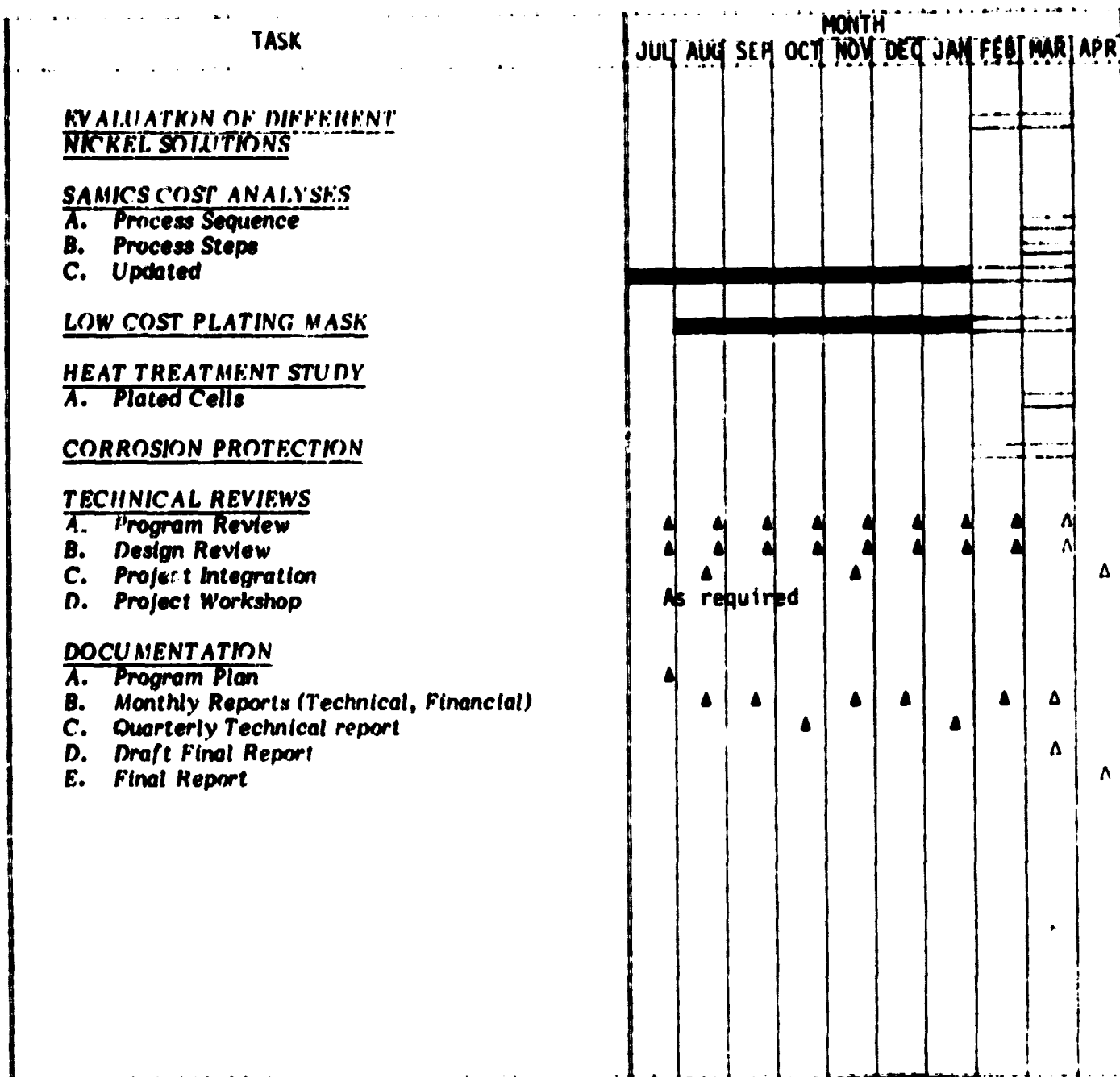
1. "Development of Low Cost Contacts to Silicon Solar Cells", Semi-Annual Report, JPL Contract No. 955244 (Optical Coating Laboratory, Inc., ASEC).
2. "Analysis of Copper Diffusion Through Different Metallic Barriers", Paper Study, JPL Contract No. 955244 (Optical Coating Laboratory, Inc., ASEC).

3. "Development of Low Cost Contacts to Silicon Solar Cells", Second Quarterly Report, JPL Contract No. 955244, (Optical Coating Laboratory, Inc., ASBC).

MILESTONE CHART

TASK	MONTH											
	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR		
<u>COPPER PLATING SYSTEM</u>												
A. Adhesion												
B. Contact Resistance												
C. Shadowing Effect												
D. Junction Shunting Effects												
<u>PROCESS CONTROL</u>												
A. Solution Control												
B. Effective Plating Rate												
C. Corrosion Resistance												
D. Solderability												
E. Mask Compatibility												
F. Simultaneous Deposition												
G. Scale-Up												
H. Preliminary Cost Estimate												
<u>PLATING VARIABLES</u>												
A. Different Solution Conditions												
B. Different Sensitizing Conditions												
C. Silicon Surface Preparation												
<u>CONTACT BUILD-UP</u>												
A. Reflow Soldering												
B. Electrolytic Plating												
<u>HEAT TREATMENTS</u>												
<u>SAMPLE CELLS</u>												
<u>EVALUATION TESTS</u>												
A. Plating Thickness, Rate												
B. Plating Coverage												
C. Grain Size												
D. Contact Resistance												
E. Plating Resistance												
F. Contact Adhesion												
G. Corrosion Resistance												
H. Solderability												

LEGEND: Scheduled: 
 Continuing: 
 Completed: 



LEGEND: Scheduled: 
 Continuing: 
 Completed: 

APPENDIX A

ELECTROLESS COPPER

COMMERCIAL PLATING SYSTEM

- A) Dynaplate Activator 120
- B) Dynaplate Conditioner 101
- C) Dynaplate 240 Electroless Copper

All solutions made by Thiokol/Dynachem Corporation. Use at room temperature.

This bath is used in the final contact sequence, but only Bath C. The thin layer of copper generated from this bath, makes the electrolytic copper adhere better. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX B

ELECTROLESS CHROMIUM

ELECTROLESS CHROMIUM BATHS

Bath A

Chromium Fluoride	15 gm/l
Chromium Chloride	1 gm/l
Sodium Citrate	7.5 gm/l
Sodium Hypophosphite	

The operating temperature was 85-95°C.

Bath B*

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>
Deionized Water	200 ml	1800 ml
Chromium Acetate	6 gm	42 gm
Nickel Acetate	.4 gm	28 gm
Sodium Citrate	8 gm	56 gm
Sodium Glycolate	8 gm	56 gm
Sodium Acetate	4 gm	28 gm
Sodium Hypophosphite	5 gm	35 gm

The operating Temperature was 85-90°C.

*This bath formulation was selected for the final chromium plating sequence. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated May 31, 1979.

Formulations taken from "Electroless Plating Today" by Dr. Edward B. Saubestre.

APPENDIX C

ELECTROLYTIC COPPER

ELECTROLYTIC COPPER SOLUTION

Deionized Water	1000 ml
H_2SO_4	30 ml
$CuSO_4$	200 ml

Solution used at room temperture. Cells plate $\sim .3$ microns per minute at 7 mA/cm^2 .

This solution was used in final contact sequence. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX D

ELECTROLESS PALLADIUM

MOTOROLA'S PLATING SOLUTIONS

Immersion Palladium Bath*

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>
Deionized Water	300 ml	1800 ml
PdCL	.05 gm	.3 gm
HCL	1 ml	6 ml
NH ₄ F	20 ml	120 ml

Mixed in a sonic bath and used at room temperature in the dark.

Electroless Palladium Plating Bath⁺

Deionized Water	830 ml
HCL	4 ml
PdCl ₂	2 gm
NH ₄ CL	27 gm
NAH ₂ PO ₄ ·2H ₂ O	6 gm
NH ₄ OH	160 ml

*Bath was used in final process. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated May 31, 1979.

⁺Bath only used for certain experiments. Palladium costs were too high.

APPENDIX E

CONTACT PROCEDURES

CHROMIUM-COPPER PLATED CONTACT PROCEDURE

1. Standard 2x2 cm substrates of 2 1/4" cells.
2. Photoresist and etch.
3. Immersion palladium bath (Appendix E).
 - (a) Five (5) seconds 6% HF.
 - (b) Immersion palladium bath for 5 minutes in the dark.
 - (c) Scrub cell with Q-tip, deionized water rinse.
 - (d) Remove photoresist with acetone.
 - (e) Heat treat 15 minutes at 400°C in N₂.
4. Electroless chromium bath (Appendix C).
 - (a) Five (5) seconds 6% HF.
 - (b) Deionized water rinse 5 seconds.
 - (c) Immerse cells for 15 minutes, rinse deionized water.
 - (d) Heat treat 15 minutes at 400°C in H₂.
5. Dip in 6% HF 5 seconds and then 5 seconds dip in deionized water.
6. Immerse in Dynachem electroless copper solution for 5 minutes at 35°C.
7. Plate in electrolytic copper solution for 20 minutes at (7 mA/cm²) for plating front and back simultaneously. Procedure plates 4-6 microns of dense copper.

For more detailed procedure see Process Specification Procedures, Contract No. 955244, dated May 31, 1979.

APPENDIX F

SCREENABLE MASK PROCEDURES

PRINT-ON PLATING MASK PROCEDURES

1. Add 5% by volume of the reducer ER-48073 to the ER-6055 plating resist and mix.
2. Silk screen the resist on the top surface of the cells using a 1/8" distance between the screen and the cells.
3. Dry cells under heat lamps at a 2 ft. distance for 5 minutes.
4. The cells are ready for plating.

Mask Material: ER-6055 Blue H.B. Fine Line Plating Resist

Reducer: ER-48073

Company: Colonial Printing Ink Company
180 E. Union Avenue
E. Rutherford, NJ 07073

NOTE: The mask is removed on the same step as the photoresist was removed in Appendix I (Step 3d). Only the acetone is replaced by trichlorolthene.